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PATENT SPECIFICATION

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(72) Inventors REES TERENCE KEITH BAKER, ROBERT JOHN
WAITE and RONALD BRIAN THOMAS



(54) IMPROVEMENTS IN OR RELATING TO CARBON FILAMENTS

(71) We, UNITED KINGDOM
ATOMIC ENERGY AUTHORITY, London,
a British Authority, do hereby declare the
invention, for which we pray that a patent
may be granted to us, and the method by
which it is to be performed, to be particu-
larly described in and by the following state-
ment:—

This invention relates to a method of grow-
ing carbon filaments.

It is known to grow carbon filaments of
less than 10 microns length by decomposition
acetylene on a catalyst in the form of metal
particles carried by an inert substrate (see,
for example, Journal of Catalysis 26, 51—62
(1972)). The filaments are observed to grow
beneath the particles, which ultimately lose
contact with the substrate. It is believed that
this mode of formation arises from a tempera-
ture gradient created by exothermic decom-
position of the acetylene to carbon and diffu-
sion of the carbon down the temperature grad-
ient and through the particles so that precipi-
tation of carbon at the rear of the particles
builds up a deposit of carbon, constituting the
filaments, and forces the particles away from
the substrate. The structure of such filaments
is believed to be partly graphitic with a core
of amorphous carbon.

We have now found that the above known
method may be improved by controlling cer-
tain process parameters within defined ranges.

Thus, the present invention provides a
method of growing carbon filaments which
comprises decomposing an acetylene or a di-
olefin to give carbon on a catalyst for the
decomposition in the form of particles which
are carried by an inert substrate, the decom-
position being carried out at a temperature
within the range from 675°C to 775°C and
at an acetylene or diolefin pressure within the
range from 0.5 mm Hg to 200 mm Hg; the
acetylene or diolefin being an acetylene or
diolefin which is exothermically decomposable
to carbon under the above conditions and the
particles being permeable to carbon under the
above conditions.

The specific conditions of temperature and
pressure in the present method may, quite
surprisingly, give rise to a considerable im-
provement in filament diameter and in number
of individual fibres per filament compared with
the abovementioned known method wherein
those specific conditions are not used. We
have found that the temperature range of
675°C to 775°C is independent of pressure
within the above stated pressure range. Our
preferred temperature range is from 700°C
to 750°C.

If the pressure is greater than 200 mm Hg,
polymerisation may take place and may in-
deed take place within the above stated range.
Thus, we prefer that the pressure is in the
range from 0.5 mm Hg to 100 Hg.

By "acetylene" we include acetylene itself
(C₂H₂) and also substituted acetylenes, though
we prefer to use acetylene itself. The preferred
diolefin is 1,3 - butadiene.

We have obtained our best yields of carbon
filaments when the acetylene or diolefin is
passed over the particles and at flow rate
in the range from 10 ml/min to 40 ml/min.
Flow rates outside of this range have been
found to give inferior yields.

In this context, we have also found
that it may be advantageous to pre-heat the
acetylene or diolefin before passing over the
particles. Thus, we have found that there is
a dramatic increase in yield when acetylene
itself is preheated to a temperature in the
range from 100°C to 750°C, preferably 550°C
or 650°C, before being passed over the par-
ticles. This advantage appears to be indepen-
dent of the nature of the catalyst particles. We
have also found that pre-heating of acetylene
may give rise to a dramatic increase in the
surface areas of the filaments produced.

The acetylene or diolefin used in the pre-
sent method may contain additives such as
free chlorine, free oxygen or free hydrogen.
The presence of such additives may give rise
to particular benefits. For example, the pre-
sence of hydrogen may increase the surface
areas of the filaments produced.

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rate, and reaction time. We found that the yield/reaction temperature pattern was independent of acetylene pressure over the range 6 to 100 torr; the highest yields were obtained at a flow rate of 30 cc/minute in a tested range of 18 to 150 cc/minute; and that highest yields were obtained for a reaction time of 30 minutes in a tested range of 5 to 180 minutes.

Example 10.

The general procedure of Example 1 was repeated using a stainless steel mesh substrate which was cleaned, before deposition of the cobalt, by ultrasonic agitation in an acetone bath. The yield of filaments using the mesh was obtained by measuring weight gain after reaction and checked against the weight loss after oxidation of the carbonaceous deposit in air (760 torr) at 600°C for 2 hours. The products were examined in the electron microscope to ensure that all the carbonaceous deposit was indeed filamentous in nature.

We carried out the example by passing acetylene, which had not been pre-heated, at 30 torr over the cobalt coated stainless steel mesh (0.9418 g) at 750°C for 30 minutes at 30 cc/minutes. We obtained a % weight increase of 2.245%, due to deposition of carbon filaments.

The procedure of Example 10 was repeated in Example 11 to 23 but at an acetylene pressure of 60 torr and where the acetylene had been pre-heated.

The results are summarised in the table below.

Example	Pre-Heating Temperature °C	% Weight Increase
11	350	1.72
12	400	2.27
13	450	4.24
14	500	4.67
15	525	4.95
16	550	5.55
17	575	4.43
18	600	3.28
19	625	3.05
20	650	6.02
21	675	5.52
22	700	4.24
23	750	2.89

The results, compared with those for Example 10, clearly show the value of pre-heating, particularly at the temperatures of 550°C and 650°C respectively.

Example 10 was also repeated with various amounts of hydrogen added to the acetylene. This was found to have little effect on the ultimate yield of carbon filaments.

Example 24.

The procedure of Examples 11 to 23 were repeated using a stainless steel mesh manufactured by a photo-etch technique and thus having a highly polished surface. Filament yields of 12 to 16%, weight were obtained.

WHAT WE CLAIM IS:—

1. A method of growing carbon filaments which comprises decomposing an acetylene or a diolefin to give carbon on a catalyst for the decomposition in the form of particles which are carried by an inert substrate, the decomposition being carried out at a temperature within the range from 675°C to 775°C and at an acetylene or diolefinic pressure within the range from 0.5 mm Hg to 200 mm Hg, the acetylene or diolefin being an acetylene or diolefin which is exothermically decomposable to carbon under the above conditions and the particles being permeable to carbon under the above conditions.

2. A method according to claim 1 wherein the decomposition is carried out at a temperature within the range from 700°C to 750°C.

3. A method according to either of the preceding claims wherein the pressure is within the range from 0.5 mm Hg to 100 mm Hg.

4. A method according to any of the preceding claims wherein the acetylene is acetylene itself (C_2H_2).

5. A method according to any of claims 1 to 3 wherein the diolefin is 1,3 - butadiene.

6. A method according to any of the preceding claims wherein the acetylene or diolefin is passed over the particles at a flow rate in the range from 10 ml/minute to 40 ml/minute.

7. A method according to claim 4 wherein the acetylene (C_2H_2) is pre-heated to a temperature in the range from 100°C to 750°C and is then passed over the particles.

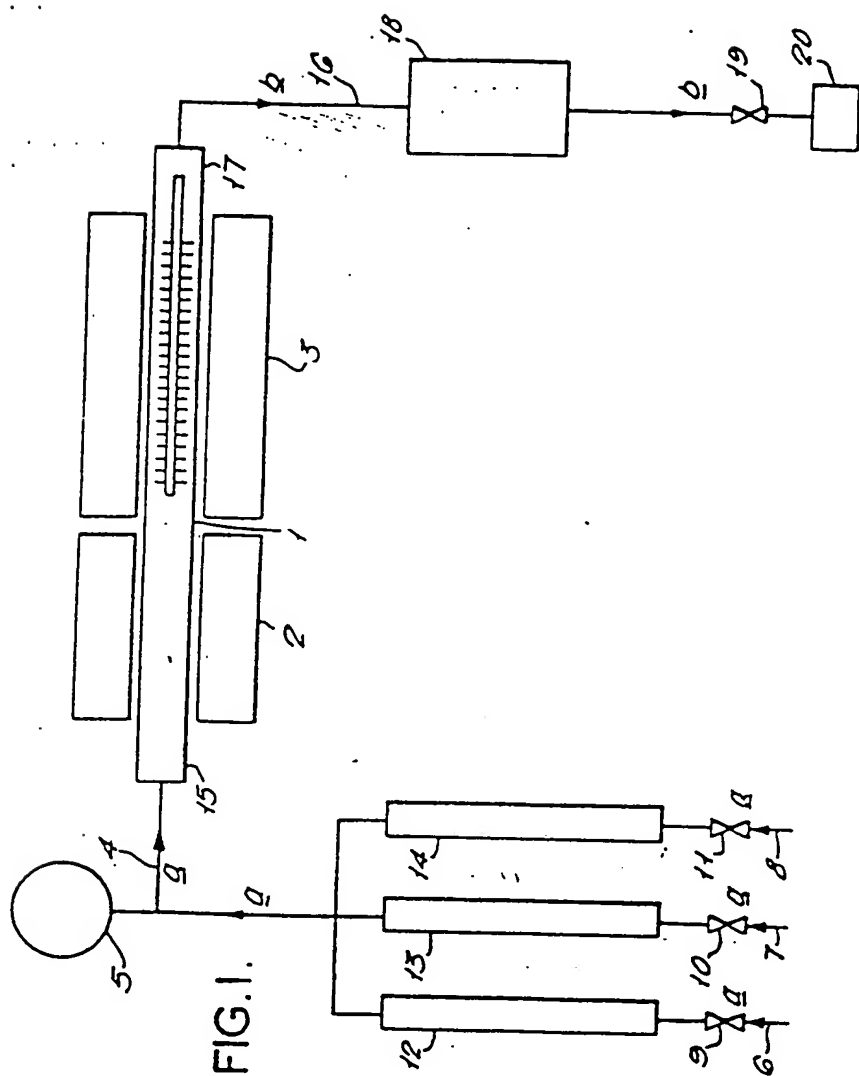
8. A method according to claim 7 wherein the temperature is 550°C.

9. A method according to claim 7 wherein the temperature is 650°C.

10. A method according to any one of the preceding claims wherein the acetylene or diolefin additionally contains free chlorine, free oxygen or free hydrogen.

11. A method according to any of the preceding claims wherein the particles are made of a transition metal.

12. A method according to claim 11 wherein the transition metal is iron, cobalt or nickel.



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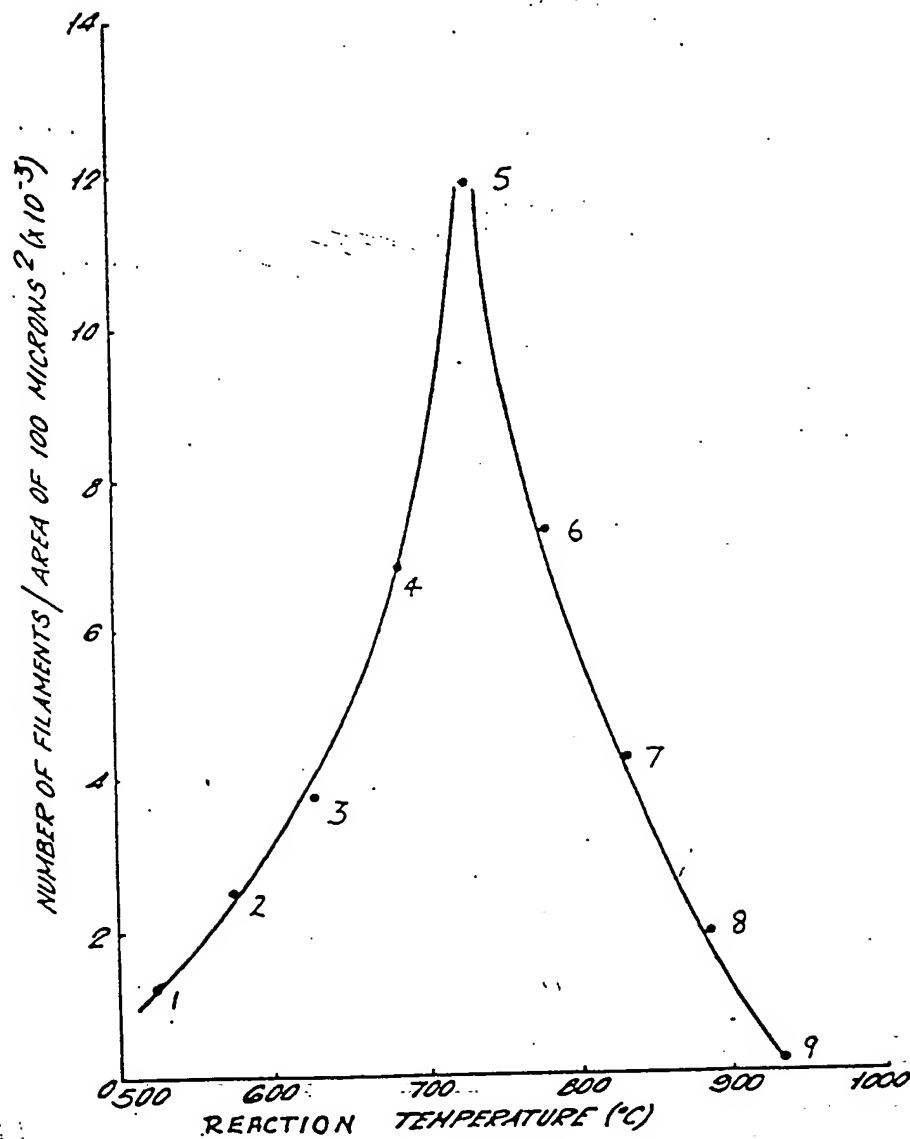
PROVISIONAL SPECIFICATION

3 SHEETS

This drawing is a reproduction of
the Original on a reduced scale

Sheet 2

FIG. 2.



13. A method according to claim 11 or claim 12 wherein the substrate carries a deposited film which has nucleated to produce the particles.

5 14. A method according to any of claims 11 to 13 wherein the particles have a mean diameter in the range from 100 Å to 1 µ.

10 15. A method according to any of the preceding claims wherein the substrate is fabricated of stainless steel.

16. A method of growing carbon filaments

substantially as described herein with reference to any of Examples 4, 5, 6 and 10 to 24.

17. Carbon filaments grown by a method 15 according to any of the preceding claims.

18. A catalyst system comprising a catalytic material carried by carbon filaments according to claim 17.

K. R. MANSELL,
Chartered Patent Agent,
Agent for the Applicants.

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In the present method, the catalyst may, for example, comprise a transition metal such as cobalt, iron or nickel, or an alloy thereof, and is preferably cobalt. The catalyst may, for example, have been deposited on the substrate in the form of a thin film which has nucleated to produce the particles. The size of the particles governs, to some extent, the diameter of the carbon filaments produced. The particles may, for example, have a mean diameter in the range from 100 Å to 1 μ.

The inert substrate is advantageously as smooth as possible and is preferably made from a very smooth stainless steel, for example, in the form of a gauze. We have obtained our best yields with a very smooth stainless steel substrate, possible because the catalyst nucleates more easily on such a substrate.

The present invention also includes carbon filaments grown by the present method.

The carbon filaments produced by the present method may have applications as strengthening materials and possibly as selective absorption agents. They are however particularly useful as catalyst support materials and this invention also includes a catalyst system comprising a catalytic material carried by carbon made by the method of the present invention. The catalytic material may, for example, be a hydrogenating catalyst such as palladium and platinum. We have deposited platinum onto carbon filaments made by the present method by immersion in a chloroplatinic acid solution followed by treatment with hydrogen, according to a known method. We tested the catalytic system produced on the hydrogenation of benzene to cyclohexane and preliminary results have shown that when a 1% benzene/hydrogen mixture at 1 atm is passed over the catalyst at 180°C conversions of up to 90% cyclohexane are attained after a single pass, the reaction being followed by a gas chromatographic procedure.

The invention will now be particularly described in Examples 4, 5, 6 and 10 to 24 below. Examples 1, 2, 3, 7, 8 and 9 are comparative examples and not examples of the invention. The examples were carried out in the apparatus depicted in Figure 1 of the drawings accompanying the Provisional Specification which is a schematic view of the apparatus.

Referring to Figure 1, a silica reaction tube 1 is surrounded by a preheating furnace 2 and by a main furnace 3. A gas feed line 4 enters one end 15 of the reaction tube 1 and is connected to a barometrically compensated pressure gauge 5. The feed line 14 is supplied by three supply lines 6, 7 and 8 each of which has a needle valve 9, 10 and 11 and a rotameter gauge 12, 13 and 14. A gas exit line 16 leaves the other end 17 of the reaction tube 1 and is connected to a Cartesian Manostat (Registered Trade Mark) 18, a needle valve 19 and a vacuum rotary pump 20. Also,

the reaction tube 1 is provided at several points with chromel/aluminel thermocouples (not shown).

In the operation of the apparatus shown in Figure 1, a specimen to be treated is placed in the section of the reaction tube 1 bounded by the main furnace 3. This section is then raised to the required reaction temperature by means of the main furnace 3. The pump 20 is switched on and gases are passed along the supply lines 6, 7 and 8, through the needle valves 9, 10 and 11 and the rotameter gauges 12, 13 and 14, and along the feed line 4 into the reaction tube 1 as shown by the arrows *a*. If required, the gases are heated in the tube 1 by means of the preheat furnace 2. The gases pass over the specimen and then out of the tube 1 via the gas exit line 16, whence they pass through the monostat 18 and the valve 19 to the pump 20. The pressure is maintained at a pre-determined level by means of the monostat 18 and the pump 20. This level is measured on the gauge 5. Gas flow rate values are controlled by the valves 9, 10 and 11 and are obtained from the rotameters 12, 13 and 14 and tube temperature values from the thermocouples (not shown).

Example 1.

Spectographically pure cobalt was evaporated onto a graphite substrate at 10⁻² torr from a tungsten filament to produce a continuous film of cobalt at least one atom thick.

The cobalt carried by the substrate, constituting the specimen to be treated, was placed in the reaction tube 1 of the apparatus shown in Figure 1 and was heated to a reaction temperature of 525°C. Acetylene gas, at a pressure of .6 torr, and which was not pre-heated, was then passed over the cobalt for 10 minutes. Carbon filaments were formed by decomposition of the acetylene on the cobalt.

The number of filaments per unit area of substrate surface was measured and also the mean filament diameter.

Examples 2 to 9.

The procedure of Example 1 was repeated but at different temperatures. The results are summarised in the graphs shown in Figures 2 and 3 of the drawings accompanying the Provisional Specification where the Example numbers are indicated against the points on the graphs. Figure 2 shows the relationship between the number of filaments per unit area and reaction temperature, and Figure 3 shows the relationship between mean filament diameter and reaction temperature. It should be noted that there is no value for Example 9 in Figure 3. These results clearly show the advantages of selecting a temperature in the range from 675°C to 775°C as in our invention.

We repeated Examples 1 to 9 to determine the effects of acetylene pressure, acetylene flow

FIG. 3.

